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D2

(11) Publication number:

0 228 885

A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86309990.9

(51) Int.Cl.: B 01 J 35/02

(22) Date of filing: 22.12.86

(30) Priority: 28.12.85 JP 299545/85

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(43) Date of publication of application:
15.07.87 Bulletin 87/29

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(54) Designated Contracting States:
DE FR GB

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(54) Porous membrane for use in reaction process.

(57) A porous membrane (11) adapted for use in a reaction process, the porous membrane or a porous layer therein being formed with interconnected micropores having an average pore size less than 100 nm and containing uniformly distributed therein a catalytic component such as molybdenum sulfide, platinum-alumina or palladium-silica-alumina.

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POROUS MEMBRANE FOR USE IN REACTION PROCESS

The present invention relates to a porous membrane adapted for use in a chemical reaction process.

In the field of gas-separation in which a gas diffusion method is adapted to separate a specific gas from a mixture of gases, there has been utilized a porous membrane which is formed with interconnected micropores having an average pore size of between several ten Å and several hundred Å, smaller than mean free path of gas molecules. In Japanese Patent Early Publication No. 59-59223, disclosed is such a porous membrane adapted to separate hydrogen gas from a mixture of hydrogen and nitrogen or carbon monoxide the molecular weight ratio of which is relatively large. The separation of hydrogen gas from the mixture is carried out by a difference in rate of permeability between the gases in Knudsen flow.

In recent years, it has been found that the characteristic of the porous membrane in gas-separation is useful for a chemical reaction process. In the case that a reaction rate in a catalytic reaction process ($A + B + P$) is noticeably decreased due to a pressure of product gas P or the reaction is restricted by equilibrium, the porous membrane is effective to exhaust the product gas P from the reaction system therethrough thereby to enhance percent conversion of the product gas and efficiency in separation and concentration of the product gas P . On Pages 58-61 of Chemical Engineering issued on February, 1984, such a reaction process is disclosed as a decomposition reaction process of hydrosulfide ($H_2S = H_2 + S$), wherein as shown in Fig. 7, the porous membrane is in the form of a porous glass pipe 1 which is filled with catalytic particles 2 of molybdenum sulfide to effect decomposition reaction of raw material gases supplied therein and to concentrate the product gas dependent upon a difference in pressure between the interior and exterior of pipe 1.

In the reaction process described above, however, sufficient separation of the product gas may not be effected due to insufficient membrane area in a volume unit of the porous membrane and insufficient contact of the product gas with the porous membrane. This results in low percent conversion of the product gas.

Additionally, the presence of catalytic particles 2 results in an increase of a pressure loss of the raw material gases passing through the glass pipe 1, and the pores of glass pipe 1 are clogged with powder of the 5 catalytic particles.

It is, therefore, a primary object of the present invention to provide a porous membrane capable of enhancing the percent conversion of the product gas in the chemical reaction process and efficiency in 10 separation and concentration of the product gas without causing any problems as described above.

According to the present invention, the primary object is attained by providing a porous membrane formed with numerous interconnected micropores and being 15 superior in selective permeability and catalytic activity. The porous membrane is in the form of a single layer porous membrane which is formed with numerous interconnected micropores having an average pore size less than 1000 Å and contains therein a catalytic 20 component such as molybdenum sulfide, platinum-alumina, palladium-silica-alumina or the like essentially in a uniform condition. Alternatively, the porous membrane may be in the form of a multiple layered porous membrane which is composed of a porous support formed with 25 numerous interconnected micropores, at least a porous

thin layer integrally formed on the porous support and being formed with numerous interconnected micropores having an average pore size less than that of the micropores in the porous support, wherein the average 5 pore size of the micropores in the porous thin layer is determined to be essentially less than 1000 Å, and either the porous support or the porous thin layer contains therein the catalytic component essentially in a uniform condition.

10 For a better understanding of the present invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings, in which:

15 Figs. 1 to 5 schematically illustrate respective enlarged cross-sections of porous membranes in accordance with the present invention;

Fig. 6 (a) is a sectional view of a reaction apparatus in which the porous membranes each are utilized as a module of the apparatus;

20 Fig. 6 (b) is a front view of the reaction apparatus depicted along arrows in Fig. 6 (a); and

Fig. 7 is a sectional view of a conventional reaction apparatus.

In Fig. 1 of the drawings, there is 25 schematically illustrated a single layer porous membrane

11 which is formed with numerous interconnected micropores having an average pore size less than 1000 Å and contains therein a catalytic component essentially in a uniform condition. For use in a chemical reaction

5 process under relatively high temperature and pressure, it is preferable that the porous membrane 11 is made of an inorganic raw material such as alumina, silica-alumina, zirconia, zeolite, porous glass, carbon or the like. To uniformly contain the catalytic

10 component in the porous membrane, the inorganic raw material is uniformly mixed with the catalytic component raw material by means of a coprecipitation method or a kneading method and is formed in a desired configuration. Alternatively, the inorganic raw material is

15 preliminarily formed in a desired configuration and is added thereto the catalytic component raw material by means of an impregnation method, an adsorption method or an ion-exchange method. In this embodiment, a supported precious metal catalyst such as platinum-alumina,

20 palladium-silica-alumina or the like may be used as the catalytic component raw material in accordance with the chemical reaction process. In use of the porous membrane 11 in a decomposition reaction process of hydrosulfide, molybdenum sulfide is used as the catalytic component raw

25 material. In this case, it has been found that the average pore size of the micropores in porous membrane 11 is closely related to selective gas permeability.

For this reason, it is desirable that in use of the porous membrane 11 under high temperature and pressure, the average pore size is determined to be less than 200 Å.

- 5 In Fig. 2 there is schematically illustrated a double layered porous membrane 12 which is composed of a porous support 12a and a porous thin layer 12b integrally formed on the porous support 12a and containing therein a catalytic component essentially in a uniform condition.
- 10 Similarly, Fig. 3 illustrates another double layered porous membrane 13 which is composed of a porous support 13a containing therein a catalytic component essentially in a uniform condition, and a porous thin layer 13b integrally formed on the porous support 13a. In the
- 15 double layered porous membranes 12 and 13, it is preferable that the porous supports 12a, 13a each are made of an inorganic raw material such as alumina, silica-alumina, mullite, cordierite, zirconia, carbon or the like. The porous supports 12a, 13a each are formed
- 20 in a desired configuration under the same condition as a conventional forming condition of a ceramic porous support and subjected to a firing or heating treatment.
- During the forming process of the porous support 13a, the same catalytic component raw material as that of the
- 25 single layer porous membrane 11 is added to the inorganic raw material by means of the impregnation, adsorption or

ion-exchange method. The porous supports 12a, 13a each are formed with numerous interconnected micropores having an average pore size of about 0.5μ to 30μ , preferably about 0.5μ to 5μ . In this instance, the average pore size of the micropores is determined to reliably effect gas diffusion and to eliminate the occurrence of cracks or pin-holes in the porous support. From the point of view of strength and processability, it is preferable that the thickness of the porous support is determined to 10 be about 1mm.

The porous thin layers 12b, 13b each are made of the same raw material as that of the single layer porous membrane 11 and are integrally formed on one surface of the respective porous supports 12a, 13a by means of a 15 sol-gel method, a high pressure adherence method of fine powder, an adherence method of porous glass or the like. The catalytic component of the porous thin layer 12b is contained in the inorganic raw material in the same manner as that in the porous support 13a. The porous 20 thin layers 12b, 13b each are formed with numerous interconnected micropores having an average pore size less than 1000 \AA . Preferably, the thickness of the porous thin layer is determined to be less than 500μ , desirably about 10 \AA to 100μ . This is useful to 25 reliably effect gas-diffusion and to eliminate the occurrence of cracks or pin-holes in the porous thin

layer. In this respect, it has been also found that the average pore size of the micropores in respective porous thin layers 12b, 13b and the thickness of the same are closely related to selective permeability of the double layered porous membranes 12, 13. In the double layered porous membrane 12, it is advantageous that the porous thin layer 12b can be formed as thinly as possible to enhance selective permeability thereof in comparison with the single layer porous membrane 11 shown in Fig. 1. In 10 the double layered porous membrane 13, it is advantageous that the porous support 13a is useful to contain therein a sufficient amount of catalytic component so as to enhance catalytic activity of the porous membrane 13. In this sense, the porous thin layer 13a itself may be made 15 of the catalytic component.

In Fig. 4 there is schematically illustrated a triple layered porous membrane 14 which is composed of a porous support 14a, a first porous thin layer 14b integrally formed on the porous support 14a, and a second 20 porous thin layer 14c integrally formed on the first porous thin layer 14b. In the porous membrane 14, the first porous thin layer 14b contains therein the same catalytic component as that of the single layer porous membrane 11, and the second porous thin layer 14c is 25 formed to provide selective permeability. In Fig. 5 there is schematically illustrated another triple layered

porous membrane 15 which is composed of a porous support 15a, and first and second porous thin layers 15b and 15c integrally formed on the opposite surfaces of the porous support 15a. In the porous membrane 15, the first porous
5 thin layer 15b contains therein the catalytic component, and the second porous thin layer 15c is formed to provide selective permeability. The component of the respective porous supports 14a, 15a is substantially the same as that of the porous support 12a, the component of the
10 respective porous thin layers 14b, 15b is substantially the same as that of the porous thin layer 12b, and the component of the respective porous thin layers 14c, 15c is substantially the same as that of the porous thin layer 13b. In addition, the average pore size of
15 respective micropores in the first porous thin layers 14b, 15b and the thickness of the same are determined to be more than those of the porous thin layer 12b, and the second porous thin layers 14c, 15c may be modified to contain therein the catalytic component.

20 In a practical embodiment of the present invention, the pore size in the foregoing porous membranes 11-15 can be adjusted by the composition of the raw material, the mechanical treatment condition, the heat treatment condition, the firing condition or the like. For instance, the adjustment of the pore size less
25 than 1000 Å can be carried out by the following method.

In a sol-gel process for gelidifying fine sol-primary particles obtained by hydrolysis of ferro-alcoide, the sol-primary particles are merely gelidified to provide a porous body formed with numerous micropores having an average pore size less than 200 Å. To obtain a porous body with numerous micropores having an average pore size of about 200 Å to about 1000 Å, the sol-primary particles are temporarily fired at a temperature below 900°C to obtain fine powder thereof. Subsequently, an appropriate amount of the fine power is added to the sol-particles or pulverized in a dry condition to be used as a carrier slurry. In a manufacturing method of a porous glass, the average pore size in the porous membrane can be adjusted by an appropriate selection of the composition of phase-separable glass particles, a temperature of phase-separation treatment, and a melting treatment condition. In an adherence method of fine powder under a high pressure, an isostatic press method is applied to powder of particle diameter less than 1 μ to obtain a porous body formed with micropores having an average pore size less than 1000 Å.

In a practical embodiment of the present invention, the porous membranes 11-15 each are used as a desired module in the form of a plate member, a pipe element, a honeycomb structure or the like. Assuming that in such a module an mount of reaction fluid flows

along one side of the porous membrane, a chemical reaction of the fluid is caused by catalytic activity of the porous membrane such that a specific product fluid is separated from the reaction fluid and concentrated by 5 selective permeability of the porous membrane. In such use of the porous membrane, it is not necessary to contain catalytic particles within the porous membrane pipe as in the conventional reaction process. For this reason, the membrane area in a volume unit of the porous 10 membrane is increased to ensure sufficient contact of the reaction fluid with the porous membrane, a pressure loss of the reaction fluid is decreased, and clogging of the pores in the porous membrane is avoided. It is, therefore, able to enhance percent conversion of the 15 product fluid from the reaction fluid. Owing to these facts, the reaction apparatus can be constructed in a small size. Although the porous membrane can be utilized in various reaction processes for dehydrogenation reaction, hydrogenation reaction, hydrogenolysis reaction 20 and the like, it is desirable that the porous membrane is utilized in a reaction process for gas-separation, for instance, in a process for collecting hydrogen from purge gases in decomposition reaction of hydrosulfide, ammonia synthesis, methanol synthesis and the like.

25 Hereinafter, the respective manufacturing methods of the porous membranes 11-15 for use in

a decomposition reaction process of hydrosulfide will be described in detail.

Example 1

For manufacturing the porous membrane 11 in the form of a pipe element, boehmite-sol obtained by hydrolysis of aluminum isopropoxide was mixed with molybdenum sulfide having an average particle diameter of 1 μ and pulverized in a ball mill to prepare slip thereof. The slip was dried by a spray dryer, mixed with an organic binder, and formed by extrusion into a pipe element. The pipe element was dried at a temperature of 100 °C for two hours, thereafter fired at a temperature of 400 °C for three hours in the atmospheric air, and further heat treated at a temperature of 800 °C for three hours in the flow of nitrogen. The composition of the resultant pipe element is listed in a column of Example 1 on a table attached hereto.

Example 2

For manufacturing the porous membrane 12 in the form of a pipe element, the slip obtained in Example 1 was used as dipping slurry. The slurry was applied to cover the internal surface of a pipe-shaped porous support (12a) of cordierite, dried at a temperature of 100 °C for two hours, thereafter fired at a temperature of 400 °C for three hours in the atmospheric air, and futher

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heat treated at a temperature of 800°C for three hours in the flow of nitrogen to form a porous thin layer (12b) on the internal surface of the pipe-shaped porous support (12a). The composition of the resultant pipe element is 5 listed in a column of Example 2 on the table.

Example 3

For manufacturing the porous membrane 13 in the form of a pipe element, molybdenum sulfide having an average particle diameter of 1 μ was added to an organic 10 binder and formed by extrusion into a pipe-shaped element. The pipe-shaped element was dried at a temperature of 100°C for two hours, fired at a temperature of 400°C for three hours in the atmospheric air, and further heat treated at a temperature of 800°C 15 for three hours in the flow of nitrogen to obtain a pipe-shaped porous support (13a) of molybdenum sulfide. Subsequently, boehmite-sol obtained by hydrolysis of aluminum isopropoxide was applied to cover the external 20 surface of the pipe-shaped porous support (13a) and fired at a temperature of 400°C for three hours in the atmospheric air to form a porous thin layer (13b) on the external surface of the pipe-shaped porous support (13a). The composition of the resultant porous pipe element is listed in a column of Example 3 on the table.

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Example 4

For manufacturing the porous membrane 14 in the form of a pipe element, slurry A in the form of molybdenum sulfide having an average particle diameter of 5 1μ was applied to cover the internal surface of a pipe-shaped porous support (14a) of cordierite, dried at a temperature of 100°C for two hours, thereafter fired at a temperature of 400°C for three hours in the atmospheric air, and further heat treated at a temperature of 800°C 10 for three hours in the flow of nitrogen to form a first porous thin layer (14b) on the internal surface of the pipe-shaped porous support (14a). Subsequently, slurry B in the form of boehmite-sol obtained by hydrolysis of aluminum isopropoxide was applied to cover the internal 15 surface of the first porous thin layer (14b), dried at a temperature of 100°C for two hours, thereafter fired at a temperature of 400°C for three hours in the atmospheric air to form a second porous thin layer (14c) on the first porous thin layer (14b). The composition of the 20 resultant porous pipe element is listed in a column of Example 4 on the table.

Example 5

For manufacturing the porous membrane 15 in the form of a pipe element, the pipe-shaped porous support of 25 Example 4 was used as a pipe-shaped porous support (15a), and the slurry A of Example 4 was applied to cover

- the internal surface of the pipe-shaped porous support (15a), fired and heat treated in the same manner as in Example 4 to form a first porous thin layer (15b) on the internal surface of the pipe-shaped porous support (15a).
- 5 Additionally, the slurry B of Example 4 was applied to cover the external surface of the pipe-shaped porous support (15a) and fired in the same manner as in Example 4 to form a second porous thin layer (15c) on the external surface of the pipe-shaped porous support (15a).
- 10 The composition of the resultant porous pipe element is listed in a column of Example 5 on the table.

Comparative Example

A first comparative example 1 was prepared in the form of a porous pipe element (16) made of cordierite and filled with beads of molybdenum sulfide having an average particle diameter of 1mm. A second comparative example 2 was prepared in the form of a porous pipe element (17) made of cordierite, the external surface of which was covered by the slurry B of Example 4, fired, heat treated, and filled with the beads of molybdenum sulfide. The respective compositions of the porous pipe elements (16) and (17) are listed in each column of Comparative Examples 1 and 2 on the table.

Test

The respective porous pipe elements in the foregoing Examples 1-5 and Comparative Examples 1 and 2 were tested for decomposition reaction of hydrosulfide in 5 a reaction apparatus illustrated in Figs. 6(a) and 6(b). The reaction apparatus comprises a plurality of parallel pipe elements 10 mounted within a cylindrical casing 20. In this test, the respective porous pipe elements in the foregoing Examples were used as the parallel pipe 10 elements 10 to measure decomposition activity of them in reaction of hydrosulfide. The cylindrical casing 20 is formed at its opposite ends with an inlet port 21 and a first outlet port 22 and formed at its intermediate portion with a second outlet port 23. In use of the 15 reaction apparatus, an amount of hydrosulfide gas was supplied into the parallel pipe elements 10 through the inlet port 21 of casing 20, a mixture of sulfur gas and non-reacted hydrosulfide gas was exhausted from the first outlet port 22 of casing 20, and the product of hydrogen 20 gas was exhausted from the second outlet port 23 of casing 20. The test results given in the table were obtained by measurement of concentration of the separated hydrogen gas using a gas chromatographic adsorption under the following condition.

SV *1 : 500hr^{-1}

Pressure of supplied gas : 3.8 atm

Pressure at the second outlet port : 0.5 atm

Reaction temperature : 800 °C

5

where SV *1 represents an amount of supplied gas
per a volume unit of catalysis.

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Table

Example No.	Membrane	Thickness	Pore Size	MoSx *2	H ₂ *4
1	11	1mm	100 \AA	30	9.5
2	12	12a	1mm	5 μ	10.5
		12b	100 μ	100 \AA	
3	13	13a	1mm	0.5 μ	12.2
		13b	50 μ	50 \AA	
4	14	14a	1mm	5 μ	12.5
		14b	100 μ	0.5 μ	
		14c	50 μ	50 \AA	
5	15	15a	1mm	5 μ	14.0
		15b	100 μ	0.5 μ	
		15c	50 μ	50 \AA	
Comparative Example	Membrane	Thickness	Pore Size	MoSx *3	H ₂ *4
1	16	(12a)	1mm	5 μ	3.5
2	17	(12a)	1mm	5 μ	7.8
		(14c)	50 μ	50 \AA	

Note: *2: wt. % of molybdenum sulfide

*3: beads of molybdenum sulfide

*4: vol. % of hydrogen

From the table, it will be understood that in Examples 1-5, the concentration of hydrogen gas exhausted from the second outlet port 23 was a high value. This means that the porous pipe elements in Examples 1-5 were effective to enhance percent conversion of hydrogen gas from hydrosulfide and efficiency in separation and concentration of hydrogen gas. In contrast, it will be understood that in the comparative examples 1 and 2, the concentration of hydrogen gas was a low value.

While there has been shown and described what are considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various alternations and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

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CLAIMS

1. A porous membrane formed with interconnected micropores having an average pore size less than 100 nm (1000 Å) and containing a catalytic component uniformly distributed therein.
- 5 2. A porous membrane according to Claim 1, which is made of an inorganic raw material.
3. A porous membrane according to Claim 2 which is made of alumina, silica-alumina, zirconia, zeolite, porous glass or carbon.
- 10 4. A porous membrane comprising a porous support formed with interconnected micropores, at least one porous thin layer integrally formed on the porous support and formed with interconnected micropores having an average pore size less than 100 nm (1000 Å) and less than that of the 15 micropores in the porous support, the porous support and/or the porous thin layer containing a catalytic component uniformly distributed therein.
5. A porous membrane according to Claim 4, wherein the porous support and the porous thin layer are each made 20 of an inorganic raw material.
6. A porous membrane according to Claim 5 wherein the porous support is made of alumina, silica-alumina, mullite, cordierite, zirconia or carbon and the porous thin layer is made of alumina, silica-alumina, zirconia, zeolite, porous 25 glass or carbon.
7. A porous membrane according to Claim 4, 5 or 6 wherein the porous thin layer is less than 500 µm thick.
8. A porous membrane according to any one of Claims 1 to 7 wherein the catalytic component is molybdenum sulfide.
- 30 9. A porous membrane according to any one of Claim 5 to 7 wherein the catalytic component is a supported precious metal catalyst.
10. A porous membrane according to Claim 9 wherein the supported precious metal catalyst is platinum-alumina or 35 palladium-silica-alumina.

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Fig. 3

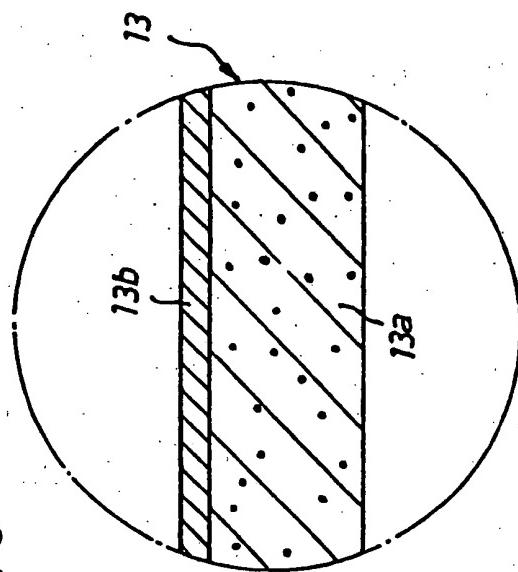


Fig. 4

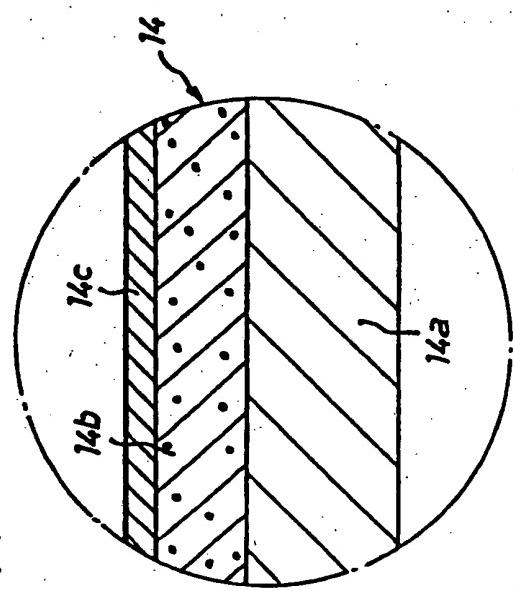


Fig. 1

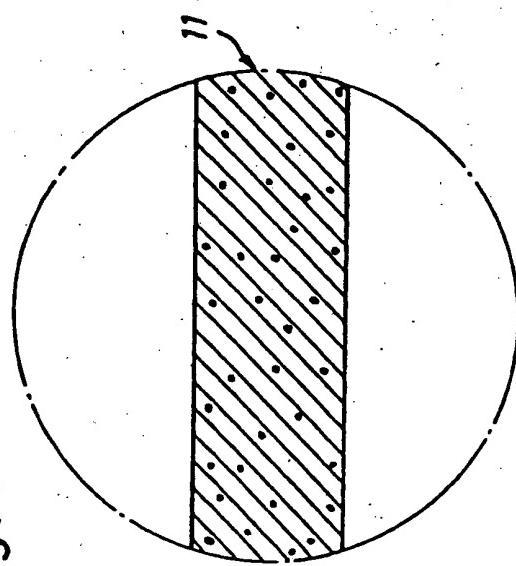
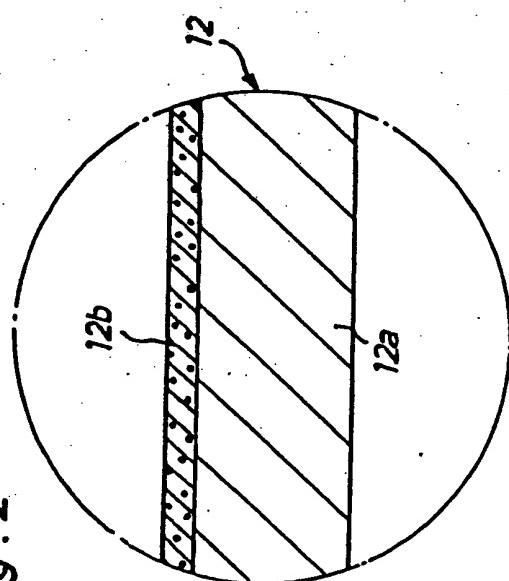


Fig. 2



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Fig. 7

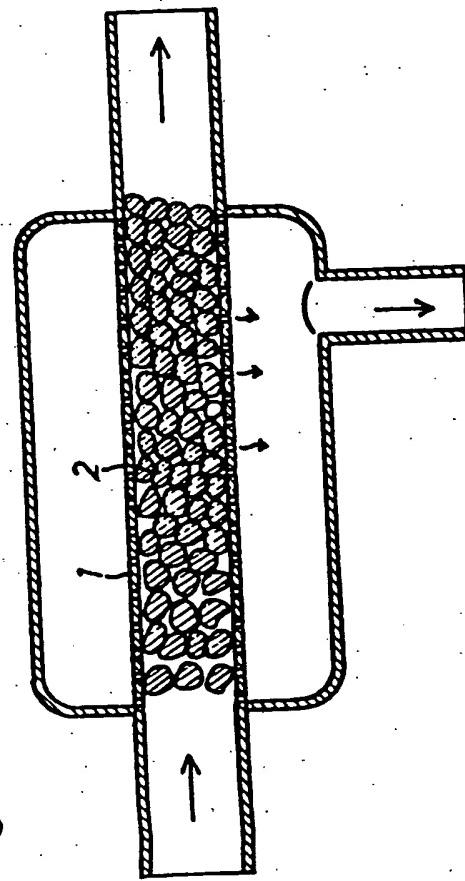


Fig. 5

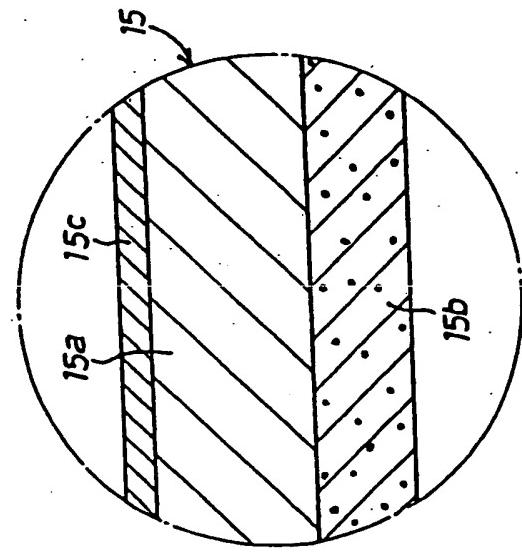


Fig. 6(b)

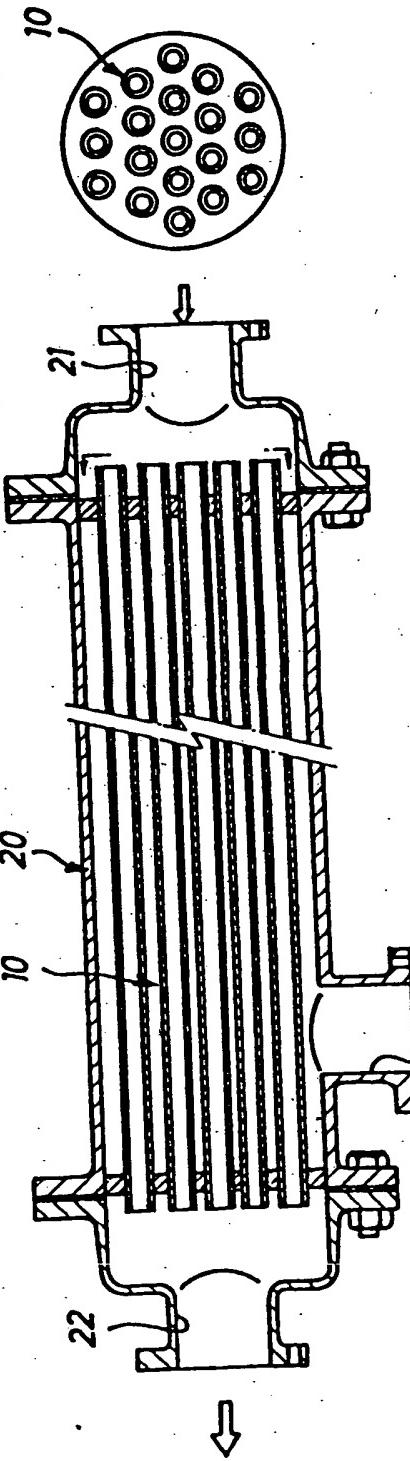


Fig. 6(a)

